# ORGANIC MICROCHEMISTRY[1]

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IN KEEPING with the policy of ANALYTICAL CHEMISTRY to continue the review of analytical chemistry on a yearly basis (*105*), the review for 1949 was prepared. As expected, the number of papers increased. Emphasis was given to methods of analysis that extend microchemical procedures for determining single compounds in mixtures. That the procedures for elemental organic analyses can be improved is shown by the large number of new and modified methods reported.

The AMERICAN CHEMICAL SOCIETY Committee on Standardization of Microchemical Apparatus critically examined different apparatus which it thinks should be standardized for the benefit of both the analyst and the manufacturer. Further collaborative work was done leading to the establishment of standard microprocedures for the Association of Official Agricultural Chemists.

## METHODS OF ANALYSIS

**Carbon and Hydrogen.** The "unpacked" tube is probably the most interesting feature of the carbon and hydrogen methods of analyses reported. Conventional copper oxide, platinum, and other catalyst fillings and asbestos separators have been eliminated, and instead quartz wool is used. Whether the quartz acts as a catalyst or merely as a heater for the passing gases is not certain. The "unpacked" tube requires a much higher rate of oxygen flow and higher combustion-tube temperatures. Colson (*15*) used 40 ml. of oxygen per minute and 800° C.; granular silver maintained at 600° C. was used to remove the halogens and sulfur, and lead dioxide held at 180° C. was used to remove oxides of nitrogen from the combustion products. Korshun and Klimova (*59*) used a similar rapid rate of oxygen flow but a temperature of 900° C. Solid samples were placed in a special microthimble; volatile liquids were put in a coiled capillary tube. "Unpacked" combustion tubes promise greater rapidity of analysis. To make the procedure generally applicable, however, further studies are required to ascertain the correct combination of size of tube, rate of oxygen flow, rate of volatilization of sample, and temperature of combustion.

Of all the microprocedures reported for carbon and hydrogen it was claimed that the packed-tube method of Fischer (*26*) offered the greatest improvement in accuracy. With his semiautomatic apparatus, sensitized catalysts, and 10- to 20-mg. samples, an accuracy of ±0.02% was reported. Lescher (*68*) described a semimicro modification, especially adapted to the analysis of liquid samples, in which the liquid was slowly vaporized and burned in a flame at the tip of an ampoule container. As in the unpacked-tube methods, the rate of oxygen flow was much higher than normal. Changes in combustion-tube filling were suggested by Bennett (*6*), who placed a 180-mm. section of "reduced" copper in front of a 150-mm. section of copper oxide, making it unnecessary to use lead dioxide with nitrogenous organic compounds. Combustion was carried out in a stream of nitrogen containing a small amount of oxygen. The reported results were high, but all were within the acceptable range. Heron (*46*) recommended an increase in the quantity of lead dioxide or a liquid absorber to remove more effectively the oxides of nitrogen. La Force, Ketchum, and Ballard (*65*) successfully analyzed carbonates, cyanides, and alkali or alkaline-earth organic salts for carbon by covering the sample with sodium bisulfate, then performing the combustion in the usual manner.

Two new methods employing the Van Slyke–Folch wet combustion reagents for carbon were reported in which carbon is collected as barium carbonate. Farrington, Niemann, and Swift (*24*) described a method that eliminates the need for the Van Slyke manometric apparatus; Lindenbaum, Schubert, and Armstrong (*69*) changed the usual procedure to make it applicable to analyses involving isotopic carbon.

Goulden (*38*) used a macrobalance with the method of Sucharda and Bobranski. The time required for an analysis is shortened by increasing the rate of oxygen flow and the amount of copper oxide filling. The probable sources of error in the semimicromethod of ter Meulen and Heslinga were discussed by Guzman (*41*). Renard (*88*) reviewed the literature describing open and closed absorption tubes. For determination of hydrogen alone, Pepkowitz and Proud (*85*) proposed a gasometric micromethod which depends on diffusion of the hydrogen from organic and inorganic compounds from a sealed iron capsule into a simple vacuum system. Accuracies comparable with those of standard combustion procedures were reported; none of the other elements interfered.

**Nitrogen.** KJELDAHL. Report of a collaborative study by Willits and Ogg (*106*) emphasized the wide discrepancy between nitrogen values for a refractory compound (nicotinic acid) obtained by different analysts. Good nitrogen values, however, were obtained by some of the procedures. White, Secor, and Long (*104*) accurately analyzed amino acids containing refractory nitrogen by digesting with a mercury catalyst. Although there is a tendency to omit selenium, Rauen and Buchka (*87*) claimed that 1-hour digestion after the mixture clears is sufficient for lysine and proteins containing lysine if sulfuric acid containing 0.7% selenium oxide is used. One point which most workers have not stressed but which appears to be critical is the temperature of the digestion mixture.

A modification of the Parnas apparatus reported by Johanson (*51*) includes a steam jacket for distillation, removal of spent liquor, and simple construction and assembly. Machemer and McNabb (*71*) found an average error of approximately 0.1% in distillation of ammonia into 4% boric acid and titration with methyl red indicator.

Day, Bernstorf, and Hill (*19*) suggested a modification of Sobel's microaeration technique in which aeration is carried out at 70° C. Kotlyarov (*60*) proposed a new formula for calculation of nitrogen by which the colorimetric micromethod can be used to determine 10 to 100 micrograms with an accuracy of 2 to 3%.

DUMAS. Most of the changes in the Dumas procedure proposed have been in the apparatus rather than in the technique. After a critical study, Bussmann (*12*) recommended the Zimmerman method because it reduces the possibility of errors due to leakage of air into the system under reduced pressure. Heron (*46*) proposed a banded tube filling of alternate layers of coarse and fine copper oxide for volatile compounds low in nitrogen. Brancone and Fulmor (*11*) raised the temperature of the burning furnace from 700° to 900° C. to aid in the decomposition of refractory ring compounds.

Carbon dioxide generators were described by Schöniger (*89*) and Furter and Bussmann (*30*). The AMERICAN CHEMICAL SOCIETY Committee for the Standardization of Microchemical Apparatus (*16*) described a sturdy all-metal needle valve that allows the same precise control of the rate of gas flow as does the more fragile Hershberg-Southworth valve. A weight nitrometer that eliminated disassembly was described by Koch, Simonson, and Tashinian (*56*).

[1] This paper should have been included with the articles on fundamental developments in the January issue. Because of circumstances beyond control it had to be postponed until the February issue where it appeared as pages 268-71.

**Halogens.** Schumb and Radimer (*91*) reported a method for determining fluorine in volatile compounds in which the sample is decomposed with moist oxygen in a platinum tube at 1100° C. The absorption unit is saran tubing and the final measurement is made colorimetrically. Here, as in the carbon and hydrogen determinations, a high ratio of oxygen to oxidizable material is important. Lingane and Small (*70*) suggested an interesting coulometric method for determining halide ions by which either a single halide or mixtures of iodide and bromide or iodide and chloride are determined. This method measures the electricity required for the quantitative reaction of the halide ion with a silver anode having controlled potential. Kirsten (*54*) improved his titrimetric procedure for chloride and bromide ions by substituting mercuric nitrate for the mercuric acetate previously used.

Two papers described determination of bromine. One, by Alicino, Crickenberger, and Reynolds (*1*), is based on an iodometric procedure that reduces the time required for analysis. The other, by Daudel, Flon, and Herczeg (*18*), uses the Parr bomb technique to destroy organic matter so that radioactive bromine can be measured more accurately.

Spectrophotometric methods for iodine were more involved than the volumetric procedures but were applicable to the analyses of smaller amounts of iodine. Custer and Natelson (*17*) pointed out that ultraviolet spectrophotometric measurements of solutions of elemental iodine in benzene, toluene, and potassium iodide permitted determination of as little as 0.2 microgram. Shakrokh and Chesbro (*92*) measured iodine spectrophotometrically after chromic acid oxidation of organic matter, reduction by phosphorus, oxidation to the iodate by chlorine, and reduction to free iodine by potassium iodide in acid solution. Gross, Wood, and McHargue (*40*) used a similar series of reactions but added starch and measured the starch-iodine blue complex by its light absorption in the visible region.

The volumetric methods of Grangaud (*39*), Schulek (*90*), and Lacourt and Timmermans (*64*) used the reactions silver iodate and filtration, chlorine water, and Viebock and Brecher's bromine method to obtain the iodine as iodate. The iodate was determined iodometrically with thiosulfate. The method of Lacourt and Timmermans can be used for simultaneous determination of carbon, hydrogen, and iodine, but a long time is required for iodine analysis.

Intonti and Gargiulo (*50*) determined two of the three halogens (chlorine, bromine, or iodine) simultaneously from the weight of the two silver salts and from the amount of the silver used, which was determined by either gravimetric or volumetric analyses. *Metallurgia* published some critical reviews of micromethods for particular elements. One, by Beaucourt (*5*), is a review of procedures for determination of halogens.

**Sulfur.** A gravimetric method by Stragand and Safford (*99*) is simple, direct, and generally applicable to organic sulfur analysis. The sulfur trioxide from catalytic combustion of organic material is caught on silver gauze, and its weight determined; or if halogens are present, the silver sulfate is dissolved in water, and the amount of sulfur is calculated from the loss in weight.

Two methods were reported for determining sulfur in compounds in which sulfur is readily converted to the sulfide. Klimenko (*55*) used alkali to convert the sulfur in proteins and tissues to sulfide or hydrosulfide. These are converted to sulfate, which in turn reacts with barium chromate; the liberated chromic acid is measured iodometrically with thiosulfate. Acid was used by Pepkowitz (*84*) to liberate hydrogen sulfide, which was distilled into standard calcium hypochlorite; the excess hypochlorite was determined iodometrically.

Two critical reviews, one, by Lamo (*66*), of semimicromethods and the other, by Thomson (*100*), of micromethods, discuss gravimetric as well as direct and indirect volumetric methods of sulfate analysis.

**Unsaturation.** In the past, unsaturation has been determin largely by macroprocedures using halogenation methods; there have been relatively few analyses by direct hydrogenation Hydrogenation has two advantages; it is not empirical, and it is satisfactory for conjugated unsaturation, for vinyl and allyl compounds, and for double bonds that are inaccessible to halogens because of steric hindrance. Microhydrogenation is less time-consuming and less subject to interference by catalyst poisons. Ogg and Cooper (*81*) presented a simplified apparatus and procedure for quantitative catalytic microhydrogenation. For microhalogenation, Phillips and Wake (*86*) used a special reaction flask and technique. A method for determination of the iodine number of lipides in blood serum was described by Giraut-Erler and Grimberg (*32*).

**Acetyl.** Elek and Hart's method for acetyl determination was modified by Bradbury (*10*) to eliminate the sulfur dioxide correction and avoid errors due to carbon dioxide.

**Water.** Determination of water in small amounts of material, by the calcium carbide method was described by Gorbach and Jurinka (*35*). Fischer (*27*) suggested three methods for detection of water: Potassium lead iodide in gasoline when heated with a trace of moisture or water of crystallization forms yellow lead iodide and bubbles; calcium carbide emulsion in peanut oil when heated with water leads to bubbles that remain visible after cooling; and phosphoric acid formed by adding traces of water to a gasoline solution of phosphorus pentoxide and bromocresol purple causes a change in the color of the indicator.

**Alcohols.** A quantitative colorimetric microdetermination of methanol was reported by Boos (*9*) to be rapid and specific. Opfer-Schaum (*82*) detected glycerol in mixtures by forming acrolein hydrazone and determining its eutectic temperature with *p*-nitrophenylhydrazine microscopically. De Meio (*20*) described a microextraction procedure for separating phenol before determining the phenol spectrophotometrically.

**Acids.** Although organic acids are now detected and determined largely by chromatographic techniques, some purely chemical methods have been reported. Kometiani and Sturua (*57*) described a micromethod for citric acid, and Volpi (*103*) described a method for detection of succinic acid in the presence of aconitic and tricarboxylic acids.

Other micromethods reported include a polarographic method for amino acids (*74*) and a new procedure for tryptophan (*95*).

*peri*-Naphthindantrione hydrate was substituted for ninhydrin in amino acid analysis by Moubasher and Awad (*79*). Steele, Sfortunato, and Ottolenghi (*94*) applied Schneider's method to the microanalyses of nucleic acids. Tracey (*101*) developed a manometric method for measurement of uronic acids.

**Carbohydrates.** Methods for determining glucose and mannitol in blood were described by Mosto and Cavanna (*78*) and Hamburger *et al.* (*44*), respectively. Mosto and Cavanna's paper also includes a method for urea analysis in which the urea is measured by nesslerization after treatment with urease. Use of partially hydrolyzed dextran as a substitute for blood in the treatment of shock led Hint and Thorsen (*47*) to develop a micromethod for dextran in blood.

**Miscellaneous.** l-Nicotine was recovered from animal tissue and determined by Trim (*102*), who observed a linear relation between color and concentration over the range 1.5 to 20 micrograms of nicotine per milliliter of solution.

Shkitin (*93*) developed a method for identifying azo dyes o paper or thread.

Hamburger and Rasch (*43*) compared different micromethods for determining 17-ketosteroids in urine. Methods were reported for riboflavin (*29*), phosphatase (*36*), diastase (*77*), albumin (*23*), and globulin (*13*). In addition, Kunzmann (*62*) discussed the use of micromethods in the cosmetic industry, and Kretchmer (*61*) reviewed the application of micromethods lipide chemistry.

**Molecular Weight.** An isothermal diffusion method was pro-

ɔsed by Wright (*108*), in which solutions of a known and an unknown were placed on separate pieces of filter paper and left with their vapor phases in common. The molecular weight of the unknown was calculated from the weight of solvent on the two papers.

Wilson (*107*) published a comprehensive review of molecular-weight methods. With Magee (*73*), he recommended that a cloth sleeve be used on Beckman microthermometers to minimize temperature fluctuations encountered in ebullioscopic methods.

## APPARATUS

**Balances.** A submicrobalance of the torsion type and some techniques and applications were described by Ingram (*48, 49*). Stock and Fill (*98*) controlled the swings in semimicro weighings by an air jet. Feuer (*25*) discussed a new type microbalance utilizing radiation from radioactive material, with a load capacity of 25 to 50 grams per pan and with high sensitivity and stability.

**Miscellaneous.** Modifications of the horizontal burets of Conway and Benedetti-Pichler have been proposed (*45, 58, 63*), together with three new displacement-type microburets (*31, 97*). Two new stirring devices for microtitrations have been described (*14, 96*).

Several distillation apparatus have been reported for volumes from 0.1 to 4.0 ml. with improved means of fraction recoveries (*4, 7, 37, 42, 67*). Three metal block-type melting point apparatus, one gas and two electrically heated, have been described (*72, 75, 83*); all use an optical magnification system for detecting the melting point, and that of Matthews (*75*) is equipped with a cooling device. An apparatus for microsublimation using an electric light as source of heat was proposed by Meyer (*76*).

A pipet (*33*) for spray rinsing of pipets with a measured volume of liquid has been described, and the drainage of micropipets has been studied (*3*). Other apparatus include a micromuffle (*34*), high-temperature coil and ring gas burners for microcombustions (*2*), a liquid-liquid extractor (*53*), microadapters for the Evelyn colorimeter (*28*) and the Beckman pH meter (*21*), and a thermostatically controlled micropolarimeter tube (*52*). Apparatus for making vapor pressure measurements (*8, 80*) have been proposed, and a versatile microapparatus for filtration, extraction, and distillation has been designed (*22*).

## ACKNOWLEDGMENT

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